

11.2.3 Take a 100-ml aliquot of the sample and blank (unexposed  $\text{KMnO}_4/\text{NaOH}$ ) solutions, and transfer to 400-ml beakers containing magnetic stirring bars. Using a pH meter, add concentrated  $\text{H}_2\text{SO}_4$  with stirring until a pH of 0.7 is obtained. Allow the solutions to stand for 15 minutes. Cover the beakers with watch glasses, and bring the temperature of the solutions to  $50^\circ\text{C}$  ( $122^\circ\text{F}$ ). Keep the temperature below  $60^\circ\text{C}$  ( $140^\circ\text{F}$ ). Dissolve 4.8 g of oxalic acid in a minimum volume of water, approximately 50 ml, at room temperature. Do not heat the solution. Add this solution slowly, in increments, until the  $\text{KMnO}_4$  solution becomes colorless. If the color is not completely removed, prepare some more of the above oxalic acid solution, and add until a colorless solution is obtained. Add an excess of oxalic acid by dissolving 1.6 g of oxalic acid in 50 ml of water, and add 6 ml of this solution to the colorless solution. If suspended matter is present, add concentrated  $\text{H}_2\text{SO}_4$  until a clear solution is obtained.

11.2.4 Allow the samples to cool to near room temperature, being sure that the samples are still clear. Adjust the pH to between 11.7 and 12.0 with 10 N  $\text{NaOH}$ . Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the precipitate. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 500-ml volumetric flask, and dilute to volume. The samples are now ready for cadmium reduction. Pipette a 50-ml aliquot of the sample into a 150-ml beaker, and add a magnetic stirring bar. Pipette in 1.0 ml of 6.5 percent EDTA solution, and mix.

11.3 Determine the correct stopcock setting to establish a flow rate of 7 to 9 ml/min of column rinse solution through the cadmium reduction column. Use a 50-ml graduated cylinder to collect and measure the solution volume. After the last of the rinse solution has passed from the funnel into the burette, but before air entrapment can occur, start adding the sample, and collect it in a 250-ml graduated cylinder. Complete the quantitative transfer of the sample to the column as the sample passes through the column. After the last of the sample has passed from the funnel into the burette, start adding 60 ml of column rinse solution, and collect the rinse solution until the solution just disappears from the funnel. Quantitatively transfer the sample to a 200-ml volumetric flask (a 250-ml flask may be required), and dilute to volume. The samples are now ready for  $\text{NO}_2$ -analysis.

NOTE: Two spiked samples should be run with every group of samples passed through the column. To do this, prepare two additional 50-ml aliquots of the sample suspected

to have the highest  $\text{NO}_2$ -concentration, and add 1 ml of the spiking solution to these aliquots. If the spike recovery or column efficiency (see Section 12.2) is below 95 percent, prepare a new column, and repeat the cadmium reduction.

11.4 Repeat the procedures outlined in Sections 11.2 and 11.3 for each sample and each blank.

11.5 Sample Analysis. Pipette 10 ml of sample into a culture tube. Pipette in 10 ml of sulfanilamide solution and 1.4 ml of NEDA solution. Cover the culture tube with parafilm, and mix the solution. Prepare a blank in the same manner using the sample from treatment of the unexposed  $\text{KMnO}_4/\text{NaOH}$  solution. Also, prepare a calibration standard to check the slope of the calibration curve. After a 10-minute color development interval, measure the absorbance at 540 nm against water. Read  $\mu\text{g NO}_2^-/\text{ml}$  from the calibration curve. If the absorbance is greater than that of the highest calibration standard, use less than 10 ml of sample, and repeat the analysis. Determine the  $\text{NO}_2^-$  concentration using the calibration curve obtained in Section 10.4.

NOTE: Some test tubes give a high blank  $\text{NO}_2^-$  value but culture tubes do not.

11.6 Audit Sample Analysis. Same as in Method 7, Section 11.4.

## 12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

### 12.1 Nomenclature.

B = Analysis of blank,  $\mu\text{g NO}_2^-/\text{ml}$ .

C = Concentration of  $\text{NO}_x$  as  $\text{NO}_2$ , dry basis,  $\text{mg/dsm}^3$ .

E = Column efficiency, dimensionless

$K_2 = 10^{-3} \text{ mg}/\mu\text{g}$ .

m = Mass of  $\text{NO}_x$ , as  $\text{NO}_2$ , in sample,  $\mu\text{g}$ .

$P_{\text{bar}}$  = Barometric pressure, mm Hg (in. Hg).

$P_{\text{std}}$  = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

s = Concentration of spiking solution,  $\mu\text{g NO}_3^-/\text{ml}$ .

S = Analysis of sample,  $\mu\text{g NO}_2^-/\text{ml}$ .

$T_m$  = Average dry gas meter absolute temperature,  $^\circ\text{K}$ .

$T_{\text{std}}$  = Standard absolute temperature,  $293^\circ\text{K}$  ( $528^\circ\text{R}$ ).

$V_{m(\text{std})}$  = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_m$  = Dry gas volume as measured by the dry gas meter, scm (scf).

x = Analysis of spiked sample,  $\mu\text{g NO}_2^-/\text{ml}$ .

X = Correction factor for  $\text{CO}_2$  collection =  $100/(100 - \% \text{CO}_2(V/V))$ .

y = Analysis of unspiked sample,  $\mu\text{g NO}_2^-/\text{ml}$ .

Y = Dry gas meter calibration factor.

1.0 ppm  $\text{NO} = 1.247 \text{ mg NO}/\text{m}^3$  at STP.

1.0 ppm  $\text{NO}_2 = 1.912 \text{ mg NO}_2/\text{m}^3$  at STP.

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$$1 \text{ ft}^3 = 2.832 \times 10^{-2} \text{ m}^3.$$

12.2 NO<sub>2</sub> Concentration. Calculate the NO<sub>2</sub> concentration of the solution (see Section 7.2.11) using the following equation:

$$\frac{\mu\text{g NO}_2^-}{\text{ml}} = \text{g NaNO}_2 \times \frac{\text{purity, \%}}{100} \times 10^3 \times \frac{46.01}{69.01} \quad \text{Eq. 7C-1}$$

12.3 NO<sub>3</sub> Concentration. Calculate the NO<sub>3</sub> concentration of the KNO<sub>3</sub> solution (see Section 7.2.12) using the following equation:

$$\frac{\mu\text{g NO}_3^-}{\text{ml}} = \text{g KNO}_3 \times (10^3) \times \frac{62.01}{101.10} \quad \text{Eq. 7C-2}$$

12.4 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$\begin{aligned} V_{\text{m(std)}} &= V_{\text{m}} \times Y \frac{T_{\text{std}}}{T_{\text{m}}} \frac{P_{\text{bar}}}{P_{\text{std}}} \quad \text{Eq. 7C-3} \\ &= K_1 \times Y \times V_{\text{m}} \frac{P_{\text{bar}}}{T_{\text{m}}} \end{aligned}$$

Where:

K<sub>1</sub> = 0.3855 °K/mm Hg for metric units.

K<sub>1</sub> = 17.65 °R/in. Hg for English units.

12.5 Efficiency of Cadmium Reduction Column. Calculate this value as follows:

$$E = \frac{200 (x - y)}{1.0 \text{ s} \frac{46.01}{62.01}} = \frac{269.6 (x - y)}{s} \quad \text{Eq. 7C-4}$$

Where:

200 = Final volume of sample and blank after passing through the column, ml.

1.0 = Volume of spiking solution added, ml.

46.01 = μg NO<sub>2</sub><sup>-</sup>/μmole.

62.01 = μg NO<sub>3</sub><sup>-</sup>/μmole.

12.6 Total μg NO<sub>2</sub>.

$$m = 200 \left( \frac{500}{50} \right) \left( \frac{1000}{100} \right) \left( \frac{(S - B)}{E} \right) = \frac{(2 \times 10^4)(S - B)}{E} \quad \text{Eq. 7C-5}$$

Where:

500 = Total volume of prepared sample, ml.

50 = Aliquot of prepared sample processed through cadmium column, ml.

100 = Aliquot of KMnO<sub>4</sub>/NaOH solution, ml.

1000 = Total volume of KMnO<sub>4</sub>/NaOH solution, ml.

12.7 Sample Concentration.

### 13.0 Method Performance

13.1 Precision. The intra-laboratory relative standard deviation for a single measurement is 2.8 and 2.9 percent at 201 and 268 ppm NO<sub>x</sub>, respectively.

13.2 Bias. The method does not exhibit any bias relative to Method 7.

$$C = K_2 \frac{m}{V_{\text{m(std)}}} \quad \text{Eq. 7C-6}$$

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13.3 Range. The lower detectable limit is 13 mg NO<sub>x</sub>/m<sup>3</sup>, as NO<sub>2</sub> (7 ppm NO<sub>x</sub>) when sampling at 500 ml/min for 1 hour. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect NO<sub>x</sub> emissions quantitatively up to 1782 mg NO<sub>x</sub>/m<sup>3</sup>, as NO<sub>2</sub> (932 ppm NO<sub>x</sub>).

14.0 *Pollution Prevention.* [Reserved]

15.0 *Waste Management.* [Reserved]

16.0 *References*

1. Margeson, J.H., W.J. Mitchell, J.C. Suggs, and M.R. Midgett. Integrated Sampling and Analysis Methods for Determining NO<sub>x</sub> Emissions at Electric Utility Plants. U.S. Environmental Protection Agency, Research Triangle Park, NC. Journal of the Air

Pollution Control Association. 32:1210-1215. 1982.

2. Memorandum and attachment from J.H. Margeson, Source Branch, Quality Assurance Division, Environmental Monitoring Systems Laboratory, to The Record, EPA. March 30, 1983. NH<sub>3</sub> Interference in Methods 7C and 7D.

3. Margeson, J.H., J.C. Suggs, and M.R. Midgett. Reduction of Nitrate to Nitrite with Cadmium. Anal. Chem. 52:1955-57. 1980.

4. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III—Stationary Source Specific Methods. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-600/4-77-027b. August 1977.

5. Margeson, J.H., *et al.* An Integrated Method for Determining NO<sub>x</sub> Emissions at Nitric Acid Plants. Analytical Chemistry. 47 (11):1801. 1975.